VISCOSITY EVALUATION FOR GLASS AND GLASS CRYSTAL COMPOSITIONS IN THEIR FOAMING TEMPERATURE RANGE

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A method is proposed and used to calculate the viscosity of glass and glass crystal compositions in the foaming temperature range. It is determined that for the glass phase content lower than 75% the viscosity of a glass crystal composition depends on the ratio of the crystal and glassy phases and for glass phase content higher than 75% the viscosity of the composition and foaming ratio are determined mainly by the composition of the glass phase.

Key words: glass phase, viscosity, glass crystal composition, foaming.

Viscosity is one of the most important technological parameters for obtaining glass foam materials — the foaming temperature regimes depend on its values. The viscosity of melt must be $10^5 – 10^{6.5}$ dPa · sec in order for closed pores to form. The temperature of active foaming must lie in the temperature interval of the pyroplastic state of the glass powder; this state appears as a result of the softening of the glass phase. Consequently, an important technological aspect of obtaining glass foam materials is evaluating the temperature interval in which the material softens and the value of the viscosity of the melt formed during this period.

Our objective in the present work is to determine the dependence of the viscosity of the glass crystal material on the composition and temperature and to determine the temperature interval corresponding to its softened state.

The rheological properties of foam glass which is obtained by the conventional method based on glass powder have been studied thoroughly [1 – 3]. A small amount of a residual crystalline phase is present in the glass crystal material (glass granulate) used as an intermediate product for obtaining glass crystal foam articles. The presence of this residual phase affects the viscosity of the melt.

The existing methods for determining the viscosity of glass are used for molten glass at relatively high temperatures (900°C and higher). In the range where the glass is in a plastic state with viscosity $10^7 – 10^{14}$ dPa · sec the measurements are performed by pulling a glass filament or rod (Inglish viscosimeter) or by pressing an external indenter into the sample ("Saratov" viscosimeter) [4].

The special preparation of the samples does not permit using these methods for glass crystal material. For this reason, the viscosity in the softening temperature range of the glass granulate was studied by a method which we developed using an arrangement which included a heating furnace together with an apparatus (RF Patent for a usable model No. 77443) that recorded the depth to which a rod penetrates into a layer of the compacted mix depending on the amount of softening (Fig. 1). The cylindrical furnace permits raising the temperature uniformly at rates 6 – 20 K/min. The bottom of the furnace has a base which can be lowered and on which a mold holding the mix is placed. Above the furnace there is a device with an aluminum rod, on one end of which the metal rod (diameter 2.5 – 3.5 mm) can be lowered vertically into a layer of the compacted mix. A platform holding a calibrated load is located at the other end of the aluminum rod. The metal rod is mechanically tied to a motion sensor and a penetration measuring scale. The mold with the compacted mix is placed inside the furnace, which is equipped with a thermocouple; a cover made of a light material and an opening at the center, into which the rod is lowered, is placed on the surface of the mix. The relative penetration of the rod is calculated as

$$\Delta h = \frac{h_0 - h_1}{h_0} \times 100,$$

where h_0 is the initially recorded height of the sample, mm, and h_1 is the penetration depth of the rod, mm.

The relation between Δh and the temperature can be obtained by recording the penetration of the rod into the granular glass powder (5000 cm^2/g) as the powder is heated and

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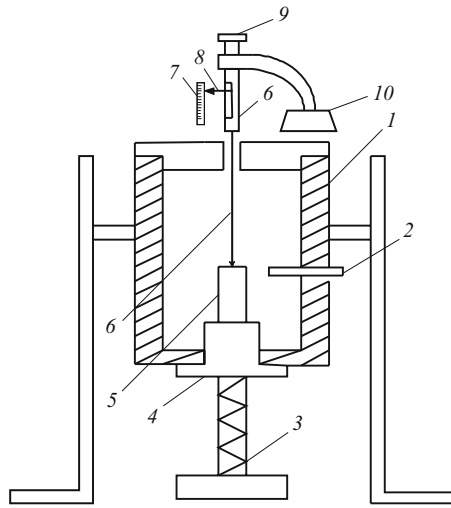[2] E-mail: kazmina@tpu.ru.

Fig. 1. Apparatus for determining the softening temperature of a material: *1*) furnace; *2*) thermocouple; *3*) setup for moving the base; *4*) mobile base; *5*) mold; *6*) rod; *7*) measurement scale; *8*) motion sensor; *9*) platform for the load; *10*) base of the measuring setup.

Fig. 2. Rod penetration versus the heating temperature: *1* and *2*) SG-1 and -2 granulates, respectively; *3*) powder of KT container glass.

softens; this relation is exponential and is distinguished by the penetration rate on the sections of the curve. The transitional stage from one horizontal line of the dependence (550 – 650°C) to another (800 – 950°C) shows the softening interval of the material, whose maximum value corresponds to the temperature t_p of its pyroplastic state.

Thus, the softening interval and the conditional temperature of the pyroplastic state can be determined for a glass crystal material with a definite composition. This is illustrated for granular glass based on zeolite rock from the Sakhaptinskoe deposit (Krasnoyarsk Krai) and marshallite from the Elbashenskoe deposit (Novosibirsk Oblast'). The component composition of the initial mixes and the chemical composition of the glass granulate are presented in Table 1; the properties of the materials are presented in [5].

Comparing the functions $\Delta h = f(t)$ shows (Fig. 2) that the temperature interval of the transition from the solid to viscous flow state is 180°C (550 – 730°C) for the glass granulate obtained on the basis of a mix consisting of zeolite and marshallite (SG-1) and 225°C (600 – 825°C) for the composition based on zeolite alone (SG-2). The softening rate of the SG-1 granulate is higher; this is recorded as a sharper ascent of the curve and higher values of Δh. The temperatures
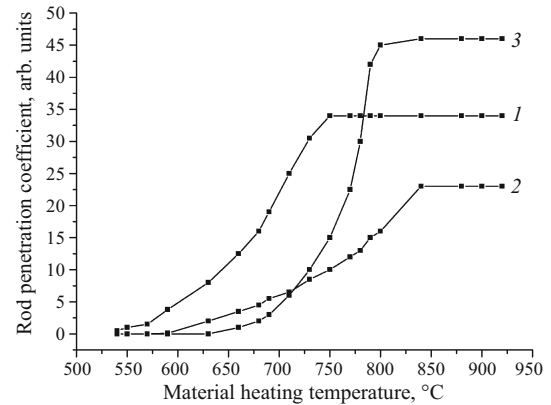
of the pyroplastic state are 730 and 825°C for the SG-1 and -2 compositions, respectively.

For purposes of making a comparison, the dependence was obtained for a powder of glass with commercial composition (brown container glass KT), whose behavior on heating differs from that of powders of granular glass with a high rate of transition into the flow state and higher values of the rod penetration coefficient (23 and 24 arb. units for glass granulate and 46 for the glass powder). The temperature of the pyroplastic state (800°C) of the glass powder falls between the values for the experimental granular glass powders.

For glass foam materials the temperature interval of active foaming as a function of the form of the foaming agent is 750 – 850°C, so that for a composition based zeolite alone the foaming process should be expected to be more active because, just as in the case of glass, the temperature of its pyroplastic state falls into this range.

The viscosity of the melt formed in the pyroplastic state [3] is, on average, $10^5 – 10^{6.5}$ dPa · sec. Taking account of the presence of a crystalline phase increases this range to 10^8 dPa · sec. Materials are considered to be high-viscosity if the viscosity of the granulate at t_p is greater than 10^8 dPa · sec and low-viscosity if less than 10^5 dPa · sec. In either case the initial composition of the mix must be adjusted in order to bring the viscosity of the melt up to optimal values and to find the appropriate temperature range for foaming.

The viscosity of the glass granulate in the softened state was determined using a calibration curve obtained for glass powder with commercial composition and well-known temperature versus viscosity characteristics. Combining the

TABLE 1.

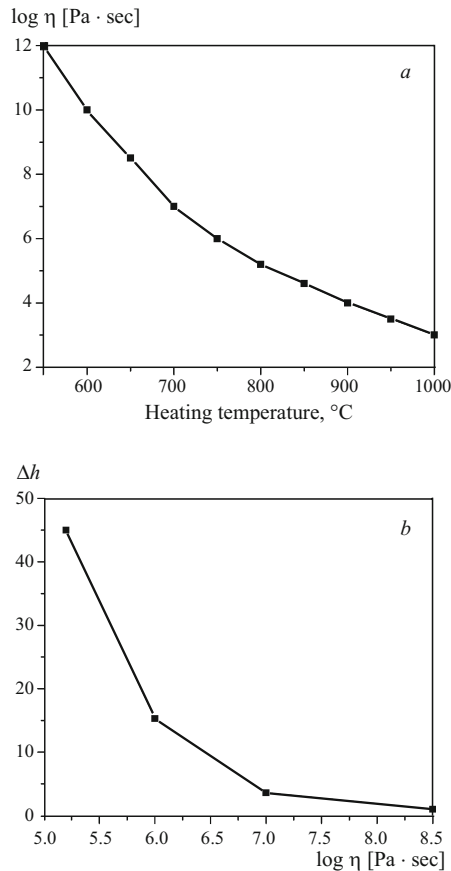| Glass granulate	Mix composition, wt.%			Glass composition, wt.%					
	zeolite	soda	marshallite	SiO_2	Na_2O	Al_2O_3	CaO	MgO	Fe_2O_3
SG-1	38	22	40	70.0	23.8	3.7	1.3	0.6	0.6
SG-2	80	20	–	61.6	17.3	13.0	4.0	1.8	2.3

Fig. 3. Temperature dependence of the logarithm of the viscosity log η of the powder of KT container glass (*a*) and the relative penetration of the rod Δh versus log η (*b*).

curve of the viscosity of glass (Fig. 3*a*) and the experimentally obtained dependence of the relative penetration of the rod into the glass powder (5000 cm^2/g) on its heating temperature gave Δh versus log η (η is the viscosity); this relation was used to find the values of the viscosity for the experimental powders (Fig. 3*b*).

Comparing the values obtained for the viscosity of the glass experimentally and by computation using the relations based on the Fulcher equation, as proposed in [4], shows that the results are in good mutual agreement; for example, the computed value of log η is 5.7 at 850°C and the experimentally measured value at the same temperature is 5.2.

Comparing the viscosity of the glass granulate with different compositions in the temperature interval 750 – 850°C shows (Table 2) that the composition with zeolite only (SG-2) has the highest values, which is also confirmed by computing its modulus of viscosity. The latter, M_v , which takes account of the chemical composition of the melt according to the relation presented below, is 1.7 for SG-2 and 1.5 for SG-1 glass granulates and 1.8 for KT glass:

$$M_v = \frac{M_{SiO_2} + 2M_{Al_2O_3}}{2M_{Fe_2O_3} + M_{CaO} + M_{MgO} + 2M_{Na_2O}},$$

where $M_{R_mO_n}$ is the mass content of the corresponding oxides, %.

It was determined that the viscosity of the glass granulate at temperatures corresponding to the pyroplastic state is $10^{6.5}$ and $10^{6.8}$ dPa · sec for SG-1 and -2, respectively, i.e., theh same as the viscosities characteristic for glass. To choose a foaming regime it is necessary to take account of the fact that the temperature of the pyroplastic state with SF-1 composition at 95°C is less than that of SG-2.

Soot was used as the foaming agent to prepare foaming mixtures from granular glass powders and to obtain samples of glass crystal foam materials for which the foaming ratio and density were determined (see Table 2). The foaming ratio was determined using the apparatus described above (the penetration rod was replaced with an indicator on the measuring apparatus). The foaming ratio (%) was calculated as

$$K_h = \frac{h_{af} - h_{bf}}{h_{bf}} \times 100,$$

where h_{bf} and h_{af} are the height of the sample before and after foaming, respectively, in mm.

Foam glass has the highest foaming ratio (85%) and the lowest density (150 kg/m^3). Comparing the properties of foam glass crystal samples obtained with granular glass showed that the SG-1 samples (based on zeolite with together marshallite) possess a lower foaming ratio and higher density. Evidently, this is due to on one hand the relatively low content of the glass phase in the glass granulate and on the other hand the fact that the temperature of the pyroplastic

TABLE 2.

Material	Experimental viscosity logarithm values at temperature, °C		Glass phase content in the glass granulate, wt.%	Foaming ratio of the foaming mix, %	Density of foamed granules, kg/m^3
	800	850			
Glass granulate:					
SG-1	5.5	5.5	75	45	350
SG-2	6.0	5.7	94	52	180
KT glass	5.3	5.2	100	85	150

state of this composition (730°C) is too low for foaming when soot is used as the foaming agent.

The quantitative estimate of the viscosity of the glass and glass crystal compositions in the foaming temperature interval makes it possible to establish the following properties.

The viscosity of the glass crystal composition in the foaming temperature range (800 – 850°C) is higher than that of glass because of the presence of a residual crystalline phase (in the form of SiO_2), which increases the viscosity of the composition, in the glass granulate.

For glass phase content below 75% in the glass crystal composition the latter's viscosity depends on the ratio of the crystalline and glass crystal phases and, vice versa, above 75% it is primarily the composition of the glass phase that determines the viscosity of the composition.

As the modulus of viscosity of the glass phase of a glass crystal composition increases from 1.5 to 1.8, the foaming ratio in the temperature interval 800 – 850°C increases from 45 to 85% because the SiO_2 and Al_2O_3 content in the glass increases.

REFERENCES

1. I. I. Kitaigorodskii and P. I. Keshishyan, *Foam Glass* [in Russian], Promstroiizdat, Moscow (1953).
2. F. Shil, *Foam Glass* [Russian translation], Stroiizdat, Moscow (1965).
3. B. K. Demidovich, *Foam Glass* [in Russian], Nauka i Tekhnika, Minsk (1975).
4. G. F. Povitkov, *Calculations in the Production of Building Glass*, Saratov (2004).
5. Yu. V. Popletneva, V. I. Vereshchagin, and O. V. Kaz'mina, "Foam glass crystal materials based on natural aluminosilicate raw materials," in: *Modern Engineering and Technologies: Proc. 14th International Scientific – Applications Conf. of Students, Graduate Students, and Young Scientists* [in Russian], Izd. Tom. Politekh. Inst., Tomsk (2008), Vol. 2, pp. 148 – 149.